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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of:	)	
	)	
Marco NAHMIAS NANNI et al.	)	Group Art Unit: 1713
	)	
Application No.: 09/878,405	)	Examiner: Peter D. Mulcahy
	)	
Filed: June 12, 2001	)	
	)	
For: PROCESS FOR PRODUCING	)	Confirmation No.: 2314
TYRES, TYRES THUS OBTAINED	)	
AND ELASTOMERIC	)	
COMPOSITIONS USED THEREIN	)	

**Attention: Mail Stop Appeal Brief-Patents**  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

**APPEAL BRIEF UNDER BOARD RULE § 41.37**

In support of the Notice of Appeal filed October 19, 2004, and further to Board Rule 41.37, Appellants present this brief and enclose herewith a check for the fee of \$340.00 required under 37 C.F.R. § 1.17(c). This Appeal Brief is timely, because it is filed within two months of the Notice of Appeal (December 19 being a Sunday).

This Appeal responds to the May 19, 2004, final rejection of claims 55-60 and 62-107.

If any additional fees are required or if the enclosed payment is insufficient, Appellants request that the required fees be charged to Deposit Account No. 06-0916.

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**REAL PARTY IN INTEREST**

Pirelli Pneumatici S.p.A. is the assignee of record for the entire right, title, and interest in the application.

**RELATED APPEALS AND INTERFERENCES**

There are currently no other appeals or interferences that will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

**STATUS OF CLAIMS**

Claims 55-60 and 62-107 are pending. Claims 1-54, 61, and 108 were previously canceled. Claims 55-60 and 62-107 have been finally rejected by the Examiner and Appellants appeal the rejection of those claims. The attached Appendix to Appeal Brief Under Rule 41.37(c)(1)(viii) contains a clean copy of the claims involved in the appeal, *i.e.*, claims 55-60 and 62-107.

**STATUS OF AMENDMENTS**

All amendments have been entered. No amendments under 37 C.F.R. § 1.116  
have been filed.

**SUMMARY OF CLAIMED SUBJECT MATTER**

The rubber product industry utilizes crosslinkable elastomeric compositions to manufacture a wide range of products including tires. *Specification* at p. 1, ll. 4-18. Conventional tire manufacturing processes, however, employ crosslinking methods, which include the use of crosslinking agents (*e.g.*, sulfur, sulfur donating compounds, peroxides, and the like), activators (*e.g.*, stearic acid, zinc oxide, and the like), and accelerators (*e.g.*, thiazoles, dithiocarbamates, thiurams, guanidines, sulphenamides, and the like). *Id.* at p. 1, ll. 22-29, p. 3, l. 13. Appellants have discovered a novel process for producing tires wherein the crosslinking step is carried out essentially without the need for additional crosslinking agents. *Id.* at p. 1, ll. 4-14.

Appellants invention, recited in independent claims 55, 62, 93, 102, 103, and 107, is generally directed to processes for producing tires for vehicle wheels (*e.g.*, claim 55), processes for preparing an elastomeric composition (*e.g.*, claims 62, 93, and 102), crosslinked manufactured products (*e.g.*, claim 103), and tires for vehicle wheels (*e.g.*, claim 107).

Claim 55 recites a process comprising the steps of: making a raw tire at least one crosslinkable elastomeric material (*specification* at p. 5, ll. 15-16); molding the raw tire in a molding cavity defined in a vulcanization mold (*id.* at p. 5, ll. 17-18; *see also, id.* at p. 22, ll. 1-27); and crosslinking the elastomeric material by heating the tire to a predetermined temperature for a predetermined time (*id.* at p. 5, ll. 19-21; *see also, id.* at p. 22, l. 28 to p. 23, l. 13); wherein the raw tire comprises at least one crosslinkable elastomeric material comprising an elastomeric polymer containing epoxide groups and



an active filler containing hydroxyl groups dispersed in the elastomeric polymer (*id.* at p. 5, ll. 22-26), said at least one crosslinkable elastomeric material has an effective degree of crosslinking equal to at least 65% after no more than 5 minutes of heating at 170 °C (*id.* at p. 6, ll. 11-15), and wherein the crosslinking step is carried out essentially without additional crosslinking agents (*id.* at p. 5, ll. 26-29).

The polymers containing epoxide groups, which can be used in the claimed inventions, are homopolymers and copolymers with elastomeric properties. They may have a T<sub>g</sub> less than 23 °C and/or 0.05 mol% of epoxide groups. *Id.* at p.10, ll. 15-28. Examples may include epoxidized diene polymers, optionally copolymerized with other monomers. *Id.* at p. 11, l. 1 to p. 14, l. 23.

“Active filler containing hydroxyl groups” means a material of inorganic or organic nature in subdivided form whose surface bears active hydroxyl groups capable of interacting with the epoxide groups of the polymer, for example silica. *Id.* at p. 14, l. 24 to p. 15, l. 28. “Effective degree of crosslinking” means, with respect to an MDR rheometric curve obtained on a sample of the composition heated at 170 °C for a total time of 30 min, the difference between the effective torque and the minimum torque values. *Id.* at p. 8, ll. 16-23; see also, *id.* at p. 8, l. 23 to p. 10, l. 14. To be “essentially without additional crosslinking agents” means that the crosslinkable composition is not subject to the action of other systems capable of bringing about the crosslinking, or else that other products which may be present in the composition can in themselves participate in the crosslinking reaction, but are used in amounts less than the minimum

amount required to obtain an appreciable degree of crosslinking. *Id.* at p. 7, l. 27 to p. 8, l. 7; *see also, id.* at p.8, ll. 7-15.

Claim 62 recites a composition comprises an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups dispersed in the elastomeric polymer (*id.* at p. 6, ll. 25-29), the composition being crosslinkable essentially without additional crosslinking agents and having an effective degree of crosslinking equal to at least 65% after no more than 5 minutes of heating at 170 °C (*id.* at p. 6, l. 29 to p. 7, l. 3).

Claim 93 recites a process for preparing an elastomeric composition comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups dispersed in the elastomeric polymer (*id.* at p. 7, ll. 15-20), the elastomeric composition being crosslinkable without additional crosslinking agents (*id.* at p. 7, ll. 20-21), the process comprising the step of mixing the active filler with the elastomeric polymer for a predetermined time (*id.* at p. 7, ll. 22-23; *see also, id.* at p. 18, ll. 21-29), to obtain a degree of dispersion of the active filler greater than 90% (*id.* at p. 7, ll. 23-25), and at a predetermined temperature (*id.* at p. 19, ll. 14-18), to avoid pre-crosslinking of the elastomeric composition (*id.* at p. 7, ll. 25-26; *see also, id.* at p. 19, ll. 1-13).

Claim 102 recites a process for preparing an elastomeric composition that comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups dispersed in the elastomeric polymer (*id.* at p. 7, ll. 15-20), the elastomeric composition being crosslinkable without additional crosslinking agents

(*id.* at p. 7, ll. 20-21), and wherein said active filler is dispersed in the elastomeric polymer containing epoxide groups with a dispersion index greater than 90% (*id.* at p. 7, ll. 23-25; see also, *id.* at p. 16, l. 20 to p. 18, l. 3), the process comprising the steps of mixing the active filler with the elastomeric polymer in the form of an aqueous emulsion or a solution in an organic solvent (*id.* at p. 19, ll. 24-27; see also, *id.* at p. 19, l. 19 to p. 20 l. 1), and then separating out by precipitation a mixture of the active filler and the elastomeric polymer (*id.* at p. 19, l. 29 to p. 20, l. 4).

Claim 103 recites a crosslinked manufactured product comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups dispersed in the elastomeric polymer (*id.* at p. 7, ll. 4-9), wherein the manufactured product is crosslinked essentially without additional crosslinking agents (*id.* at p. 7, ll. 9-11), and wherein the active filler is dispersed in the elastomeric polymer with a dispersion index greater than 90% (*id.* at p. 7, ll. 11-13; see also, *id.* at p. 16, l. 20 to p. 18, l. 3).

Claim 107 recites a tire for vehicle wheels, including one or more components made of crosslinked elastomeric material (*id.* at p. 6, ll. 17-19), wherein at least one of the components comprises a crosslinked elastomeric material comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups dispersed in the elastomeric polymer (*id.* at p. 6, ll. 19-23), the elastomeric material being crosslinked essentially without additional crosslinking agents (*id.* at p. 6, ll. 23-24), and wherein the crosslinkable elastomeric material has an effective degree of

crosslinking equal to at least 65% after no more than 5 minutes of heating at 170 °C (*id.*  
at p. 6, l. 29 to p. 7, l. 3).

**GROUND OF REJECTION**

The Examiner has rejected claims 55-60 and 62-107 as unpatentable under 35 U.S.C. § 103(a) over Varughese *et al.*, *Chemical Attraction Between Expoxidized Natural Rubber and Silica: Studies on Cure Characteristics and Low Temperature Dynamic Mechanical Properties*, Journal of Applied Polymer Science, Vol. 44, pp.1847-1855 (1992) ("*Varughese*"), or over Japanese Patent Abstract 07-090123 ("*JP 07-090123*") (collectively "The References").

### **ARGUMENT**

Appellants request that the Board reverse the final rejection of claims 55-60 and 62-107, because the claims are neither anticipated nor obvious over the cited prior art. The Examiner has rejected claims 55-60 and 62-107 as unpatentable under 35 U.S.C. § 103(a) over *Varughese* or over *JP 07-090123*. The Examiner has failed to meet his burden of establishing a *prima facie* case of obviousness with respect to any of the cited prior art.

#### **A. THE EXAMINER BEARS THE BURDENT TO ESTABLISH A PRIMA FACIE CASE OF OBVIOUSNES UNDER 35 U.S.C. § 103.**

To properly reject Appellants' claimed invention under 35 U.S.C. § 103, the U.S. Patent and Trademark Office bears the initial burden to establish a *prima facie* case of obviousness. *In re Fine* 837 F.2d 1071, 1074, 5 U.S.P.Q.2d 1596, 1599 (Fed. Cir. 1988). In other words, the Examiner bears the burden to establish each of three criteria.

First, the Examiner must establish that the references teach or suggest each and every element and limitation recited in the claims. See M.P.E.P. § 2143.03. Second, the Examiner must establish that some suggestion or motivation exists, either in the references themselves, or in the knowledge generally available to one of ordinary skill in the art, to modify the references to achieve the presently claimed invention. See M.P.E.P. § 2143.01. Third, the Examiner must establish a reasonable expectation of success for the proposed modifications. See M.P.E.P. § 2143.02. Moreover, each of these requirements must "be found in the prior art, and not be based on applicant's

disclosure.” M.P.E.P. § 2143. Appealing to “common sense” and “basic knowledge” without any evidentiary support cannot cure any deficiencies in the references. *In re Zurko*, 258 F.3d 1379, 1385, 59 U.S.P.Q.2d 1693, 1697 (Fed. Cir. 2001). If the Examiner fails to establish “a *prima facie* case of unpatentability then without more the applicant is entitled to grant of the patent.” *In re Oetiker*, 977 F.2d 1443, 1445, 24 U.S.P.Q.2d 1443, 1444 (Fed. Cir. 1992).

**B. CLAIMS 55-60 AND 62-107 ARE PATENTABLE OVER THE REFERENCES, BECAUSE THE EXAMINER HAS FAILED TO ESTABLISH A PRIMA FACIE CASE OF OBVIOUSNESS UNDER 35 U.S.C. § 103.**

In this case, the Examiner has failed to present substantial evidence establishing all three criteria. First, both references fail to teach or suggest each and every element recited in the claims. Second, there is no evidence to show that either reference or the knowledge generally available to one of ordinary skill in the art suggests or motivates the necessary modifications to the references to achieve the presently claimed invention. Third, there is no evidence of a reasonable expectation of success for the necessary modification. See M.P.E.P. §§ 2143.01 & 2143.03.

**1. Claims 55-60, 62-92, and 107 Require that the “Crosslinkable Elastomeric Material has an Effective Degree of Crosslinking Equal to at Least 65% After no More Than 5 Minutes of Heating at 170 °C.”**

Independent claims 55, 62, and 107, recite the claim limitation: “crosslinkable elastomeric material has an effective degree of crosslinking equal to at least 65% after no more than 5 minutes of heating at 170 °C.”

**a) The Rejection Should be Reversed Because the References, Either Alone or in Combination, do not Teach or Suggest the Effective Degree of Crosslinking Limitation.**

Appellants submit that neither *Varughese* nor *JP 07-090123* expressly or inherently teaches or suggests the claim limitation: “crosslinkable elastomeric material has an effective degree of crosslinking equal to at least 65% after no more than 5 minutes of heating at 170 °C.” See M.P.E.P. § 2143.03.

**(1) There is no Express Teaching of the Effective Degree of Crosslinking Limitation.**

With respect to *Varughese*, the reference teaches that a person or ordinary skill in the art would expect little or no crosslinking, under conventional vulcanization, from the mere combination of at least one crosslinkable elastomeric material comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups dispersed in the elastomeric polymer. In fact *Varughese* teaches that its process produces products that have an unacceptably low degree of crosslinking. Specifically, *Varughese* discloses that “[g]enerally, the interaction between a filler and a polymer are not high enough so that cross-linking can be detected through a rheometer torque rise.” (*Varughese* at p. 1849). This is consistent with *Varughese*’s disclosure that chemical interaction under conventionally cured silica-filled vulcanizates is comparatively poor. *Id.* This is also consistent with the disclosure that cross-linking between the epoxy and the silanol groups requires a higher activation energy than vulcanization. *Id.* Thus, *Varughese* does not disclose “an effective degree of crosslinking equal to at least 65% after no more than 5 minutes of heating at 170 °C.”



Similarly, *JP 07-090123* fails to expressly teach or suggest, at a minimum, the effective degree of crosslinking limitation. In fact, *JP 07-090123* does not address the degree of cross-linking at all.

Thus, neither reference expressly teaches or suggests this claim limitation.

**(2) There is no Inherent Teaching of the Effective Degree of Crosslinking Limitation.**

The Examiner has asserted that “[t]his is a property limitation and is presumed to be either anticipated or rendered obvious by compositions having the claimed compositional ingredients in the same amounts.” *Final Office Action* at p. 2. Appellants respectfully disagree.

The mere fact that a reference may disclose a raw tire that “comprises at least one crosslinkable elastomeric material comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups dispersed in the elastomeric polymer,” does not mean that the “at least one crosslinkable elastomeric material has an effective degree of crosslinking equal to at least 65% after no more than 5 minutes of heating at 170 °C” limitation is inherently met.

To establish inherency, the extrinsic evidence must make clear that the missing descriptive matter is necessarily present in the thing described in the reference and that it would be so recognized by persons of ordinary skill. . . .Inherency, however, may not be established by probabilities or possibilities. The mere fact that a certain thing may result from a given set of circumstances is not sufficient.

*In re Robertson*, 169 F.3d 743, 745, 49 U.S.P.Q.2d 1949, 1950-51 (Fed. Cir.

1999) (*citations omitted*); *In re Rijckaert*, 9 F.3d 1531, 1534, 28 U.S.P.Q.2d 1955, 1957

(Fed. Cir. 1993) (the fact that a certain result or characteristic may occur or be present in the prior art is not sufficient to establish inherency of the result or characteristic).

In fact, the evidence of record establishes that the mere combination of at least one crosslinkable elastomeric material comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups dispersed in the elastomeric polymer does not inherently yield a composition with the required degree of cross-linking. In particular, *Varughese* and Appellants' specification establish that not all combinations meet the effective degree of crosslinking limitation. It is merely a possibility, which is insufficient to establish inherency. See M.P.E.P. § 2143.03.

First, the effective degree of crosslinking is a function of not only the amount of recited material, but of time, temperature, and other materials. See e.g., *Specification* at pp. 22-23. Only under certain conditions may the effective degree of crosslinking be achieved. Yet, nothing in either *Varughese* or *JP 07-090123* suggests that these factors are taken into account. Thus, contrary to the Examiner's argument, the mere presence of all components (which Appellants do not concede are present) is not enough to establish inherency. Under these uncontested facts, cross-linking cannot be deemed to be inherently disclosed. See M.P.E.P. § 2112 (discussing that inherency cannot be based on what would result if conditions were optimized).

Second, as previously noted, *Varughese* admits that a person of ordinary skill in the art cannot achieve this claim limitation merely with the recited materials. *Varughese* at 1849. In fact *Varughese* teaches that its process produces products that have an unacceptably low degree of crosslinking. *Id.* Specifically, as previously discussed,

*Varughese* discloses that generally, the interaction between its filler and polymer is not high enough to be detected through a rheometer torque rise. *Id.* at 1848-49.

*Varughese's* discloses that chemical interaction under conventionally cured silica-filled vulcanizates is comparatively poor. *Id.* at 1849. Even Appellants have determined that this evidences a poor degree of cross-linking. See *Specification* at pp. 3-4.

Third, the only test data of record (Appellants' and *Varughese's*) supports the fact that this claim limitation is not inherent. Specifically, according to *Varughese* in Figure 1, the torque increase for Mix D is about 5 dN•m (8 dN•m (minimum torque) minus 13 dN•m (maximum torque)) after 1 full hour at 180 °C. *Id.* at 1849. In contrast, Appellants' Example 5 shows a near 15 dN•m increase after only 30 minutes at 170 °C. *Specification* at p. 26, Table 2. Thus, one of ordinary skill in the art would recognize *Varughese* as disclosing inadequate cross-linking for such a composition.

Moreover, Appellants have been able to calculate the effective degree of crosslinking after no more than 5 minutes of heating at 180 °C for each mixture reported by *Varughese* that does not contain additional crosslinking agents, as required by the claims. Based upon the data provided by *Varughese* in Figure 1, the effective degree of crosslinking after 5 minutes of Mix D is estimated at 6%, of Mix F is estimated at 20%, of Mix H is estimated at 0% (no crosslinking), of Mix I is estimated at 10%. See *Varughese* at. 1849, Figure 1.<sup>1</sup> These are well below the claim limitation of "at least 65% after no more than 5 minutes of heating at 170 °C." In fact, *Varughese's* values

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<sup>1</sup> Using Mix D as an example, these calculations are based on the teachings of the specification using the following values taken from Figure 1:  $M_{eff}=8.6$  dN•m at  $t_{eff}=5$  min,  $M_L=8.3$  dN•m, and  $M_{fin}=13$  dN•m.

would be even lower if the data had been collected at 170 °C, rather than 180 °C. Thus, none of *Varughese*'s compositions meet the claim limitation.

Finally, Appellants' own testing shows that the claimed limitation is not inherent. As shown by Comparative Examples 13 and 14 of Appellants' Table 4, the mere combination of the claimed elements does not inherently yield a composition with the required degree of cross-linking. See *Specification* at p. 29, Table 4. Specifically, comparative Examples 13 resulted in a 62.9% effective degree of crosslinking, and comparative Examples 14 resulted in a 53.8% effective degree of crosslinking. *Specification* at p. 29, Table 4.

Neither reference expressly teaches the claimed effective degree of crosslinking limitation. Furthermore, inherency cannot be based on the mere possibility that under some unspecified condition the desired characteristic will be found. M.P.E.P. § 2112. Accordingly, in view of the deficiencies of *Varughese* and *JP 07-090123*, the Examiner has failed to establish a *prima facie* case of obviousness and, thus, the rejection is improper and should be reversed. See *In re Brouwer*, 77 F.3d 422, 425, 37 U.S.P.Q.2d 1663, 1666 (Fed. Cir. 1996).

**b) The Rejection Should be Reversed Because the Evidence of Record Cannot Motivate a Person of Ordinary Skill in the Art to Modify the Prior Art Teachings to Meet the Effective Degree of Crosslinking Limitation.**

Neither *Varughese* nor *JP 07-090123* suggest the desirability of obtaining a "crosslinkable elastomeric material [that] has an effective degree of crosslinking equal to

at least 65% after no more than 5 minutes of heating at 170 °C". See M.P.E.P. § 2143.01

Accordingly, the Examiner must establish some motivation to modify the teachings of these references, since "[t]he fact that the claimed invention is within the capabilities of one of ordinary skill in the art is not sufficient by itself to establish a prima facie case of obviousness." M.P.E.P. § 2143. In other words, the mere fact that the references could be modified to meet the degree of crosslinking limitation does not make the modification obvious, unless the Examiner-cited evidence suggesting the desirability of such polymeric material configurations. See *In re Laskowski*, 871 F.2d 115, 11710 U.S.P.Q.2d 1397, 1398 (Fed. Cir. 1989). The Examiner, however, has not done so.

In the present case neither reference suggests the desirability of either modification. Rather, as previously noted, *Varughese* discloses that chemical interaction under conventionally cured silica-filled vulcanizates is comparatively poor. Furthermore, *JP 07-090123* fails to appreciate the property of having an effective degree of crosslinking equal to at least 65%.

Consequently, the references do not provide the requisite motivation to modify and, thus, the rejection is improper. See M.P.E.P. §2143.01.

**c) The Rejection Should be Reversed Because the Evidence of Record Cannot Establish a Reasonable Expectation of Success for the Requisite Modification of the References to Meet the Effective Degree of Crosslinking Limitation.**

The Office has not offered any reasoning as to why a beneficial result would have been expected by combining the ingredients as disclosed in *Varughese* nor *JP 07-090123* or modifying them, as needed. See M.P.E.P. § 2143.02. In fact as previously noted, *Varughese* teaches that its process produces products that have an unacceptably low degree of crosslinking, *and* that generally, the interaction between its filler and polymer are not high enough to be detected through a rheometer torque rise. *Id.* at 1848-49. This surely cannot provide a reasonable expectation of success. Moreover, in violation of the claim limitation wherein “the crosslinking step is carried out essentially without additional crosslinking agents,” *JP 07-090123* includes 0.7 phr curing promoter and 1.7 phr sulfur to achieve cross-linking. *JP 07-090123* at pp. 7-8, Table 1. Thus, teaching a person of ordinary skill in the art that such additional compounds are necessary, contrary to the claims.

Consequently, there is no evidence of a reasonable expectation of success that would prompt a person of ordinary skill in the art to make the necessary modification. See M.P.E.P. §§ 2143.01 & 2143.03.

**2. Claims 55-60, 62-92, and 107 Require that “the Crosslinking Step is Carried out Essentially Without Additional Crosslinking Agents.”**

**a) The Rejection Should be Reversed Because *JP 07-090123* Does not Teach or Suggest the Without Additional Crosslinking Agents Limitation.**

Appellants submit that *JP 07-090123* does not expressly teach or suggest the claim limitation: “crosslinkable elastomeric material has an effective degree of crosslinking equal to at least 65% after no more than 5 minutes of heating at 170 °C.” See M.P.E.P. § 2143.03.

Specifically, all of the compositions disclosed in *JP 07-090123* are cured with conventional sulfur-based vulcanizing systems. *JP 07-090123* at p. 5, ll. 21-29; *id.* at pp. 7-8, Table 1. *JP 07-090123* discloses that the sulfur content is preferably no less than 1.2 parts by weight, and more preferably from 1.5 to 3.0 parts by weight, per 100 parts by weight of rubber component. *Id.* at 5, ll. 28-29. As indicated in Table 1, page 7, the base composition of *JP 07-090123* includes 0.7 phr curing promoter and 1.7 phr sulfur. *Id.* at 7-8, Table 1. This is expressly contrary to the claim requirement that the “crosslinking step is carried out essentially without additional crosslinking agents.” See *Specification* at p. 7, l. 27 to p. 8, l. 7.

In view of the deficiencies of *JP 07-090123*, the Examiner has not and cannot meet this requirement for a case of prima facie obviousness. See M.P.E.P. § 2143.03.

**b) The Rejection Should be Reversed Because  
JP 07-090123 Teaches Away From the Without  
Additional Crosslinking Agents Limitation.**

A “reference may be said to teach away when a person of ordinary skill, upon reading the reference . . . would be led in a direction divergent from the path that was taken by the applicant.” *In re Gurley*, 27 F.3d 551, 553, 31 U.S.P.Q.2d 1130; 1131 (Fed. Cir. 1994). As discussed above, *JP 07-090123* discloses that the sulfur content is preferably no less than 1.2 parts by weight, and more preferably from 1.5 to 3.0 parts by weight, per 100 parts by weight of rubber component. *Id.* at 5, ll. 28-29. Thus, *JP 07-090123* expressly recommends violating the limitation of having “the crosslinking step is carried out essentially without additional crosslinking agents”. *JP 07-090123* at p. 7, Table 1. Moreover, a person of ordinary skilled in the art armed with *JP 07-090123* would be motivated to add crosslinking agents to achieve the cross-linking required to make its disclosed tire tread rubber composition.

**3. Claims 93 -101 Require “a Degree of Dispersion of the Active Filler Greater Than 90%, . . . at a Predetermined Temperature, to Avoid Pre-Crosslinking of the Elastomeric Composition,” and Claims 102-106 Require that “the Active Filler is Dispersed in the Elastomeric Polymer . . . with a Dispersion Index Greater than 90%.”**

Independent claim 93 includes the claimed elements a degree of dispersion of the active filler greater Than 90%, . . . at a predetermined temperature, to avoid pre-crosslinking of the elastomeric composition.” Independent claims 102 and 103 include the claimed elements “wherein the active filler is dispersed in the elastomeric polymer . . . with a dispersion index greater than 90%.” The cited prior art fails to meet



these limitations. The Examiner has not addressed either of these limitations in any Office Action, nor responded to Appellants' arguments.

**a) The Rejection Should be Reversed Because the References do not Teach or Suggest, Either Alone or in Combination, the Dispersion Limitations.**

Neither *Varughese* nor *JP 07-09123* teach or suggest, at a minimum, either dispersion limitations, as found in independent Claims 93, 102, and 103.

Again, neither reference recognizes these dispersion limits and/or the need to avoid pre-crosslinking of the elastomeric composition. In fact, *JP 07-09123* disclose that epoxidized natural rubber (ENR) does with react with silica and that the silica filler does not disperse in ENR/SBR systems. *JP 07-090123* at p. 7, ll. 30-34. It further discloses that the filler disperses well only in the presence of natural rubber (NR), which is not the claimed elastomeric polymer. *Id.* *Varughese* simply mixes the silica filler and is silent regarding the dispersive qualities of the filler. *Varughese* at 1848.

Moreover, as evidenced in *JP 07-09123* and Appellants specification, neither dispersion limitations is inherent to a disclosure of the combination of elastomer and filler. See e.g., Comparative Example 9 from Appellants' Table 3, which does not meet the dispersion requirement despite meeting the other limitations. See *Specification* at p. 28, Table 3; see also *JP 07-090123* at p. 7, ll. 30-34.

**b) The Rejection Should be Reversed Because the Evidence of Record Cannot Establish a Motivation for a Person of Ordinary Skill in the Art to Modify the Prior Art Teachings to Meet the Dispersion Limitations.**

Since *Varughese* does not recognize either of these limitations, and *JP 07-09123* only teaches the use of NR to disperse the filler, the references cannot be deemed to provide the necessary motivation to modify their teachings. See M.P.E.P. § 2143.01. Only Appellants' specification provides that information, but that is not available to the Examiner to use to meet his burden with respect to an obviousness rejection. See M.P.E.P. § 2145.X.A.

**CONCLUSION**


For the reasons given above, pending claims 55-60 and 62-107 are allowable and reversal of the Examiner's rejection is respectfully requested. The Board of Patent Appeals and Interferences should therefore reverse or dismiss the outstanding rejection and allow claims 55-60 and 62-107.

To the extent any extension of time under 37 C.F.R. § 1.136 is required to obtain entry of this Appeal Brief, such extension is hereby respectfully requested. If there are any fees due under 37 C.F.R. §§ 1.16 or 1.17 which are not enclosed herewith, including any fees required for an extension of time under 37 C.F.R. § 1.136, please charge such fees to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,  
GARRETT & DUNNER, L.L.P.

Dated: December 20, 2004

By:   
Anthony A. Hartmann  
Reg. No. 43,662



**CLAIMS APPENDIX TO APPEAL BRIEF**  
**UNDER RULE 41.37(C)(1)(VIII)**

Pending claims 55-60 and 62-107:

55. A process for producing tyres for vehicle wheels, the process comprising the steps of:

making a raw tyre comprising at least one crosslinkable elastomeric material;  
molding the raw tyre in a molding cavity defined in a vulcanization mold; and  
crosslinking the elastomeric material by heating the tyre to a predetermined temperature for a predetermined time;

wherein the raw tyre comprises at least one crosslinkable elastomeric material comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups dispersed in the elastomeric polymer, said at least one crosslinkable elastomeric material has an effective degree of crosslinking equal to at least 65% after no more than 5 minutes of heating at 170°C, and wherein the crosslinking step is carried out essentially without additional crosslinking agents.

56 The process of claim 55, wherein the crosslinking step is carried out by heating the tyre to a maximum temperature of at least 100°C for at least 3 minutes.

57 The process of claim 56, wherein the crosslinking step is carried out by heating the tyre to a maximum temperature of at least 120°C for at least 5 minutes.

58 The process of claim 55, wherein the active filler is dispersed in the elastomeric polymer containing epoxide groups with a dispersion index greater than 90%.

59 The process of claim 58, wherein the active filler is dispersed in the elastomeric polymer containing epoxide groups with a dispersion index greater than 95%.

60 The process of claim 59, wherein the active filler is dispersed in the elastomeric polymer containing epoxide groups with a dispersion index greater than 98%

62 A composition comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups dispersed in the elastomeric polymer, the composition being crosslinkable essentially without additional crosslinking agents and having an effective degree of crosslinking equal to at least 65% after no more than 5 minutes of heating at 170°C.

63 The composition of claim 62, wherein the active filler is dispersed in the elastomeric polymer containing epoxide groups with a dispersion index greater than 90%.

64 The composition of claim 63, wherein the active filler is dispersed in the elastomeric polymer containing epoxide groups with a dispersion index greater than 95%.

65 The composition of claim 64, wherein the active filler is dispersed in the elastomeric polymer containing epoxide groups with a dispersion index greater than 98%.

66 The composition of claim 62, wherein the elastomeric polymer containing epoxide groups is a homopolymer or copolymer with elastomeric properties having a glass transition temperature less than 23°C.

67 The composition of claim 66, wherein the elastomeric polymer containing epoxide groups has a glass transition temperature less than 0°C.

68 The composition of claim 62, wherein the elastomeric polymer contains at least 0.05 mol% of epoxide groups relative to a total number of moles of monomers present in the elastomeric polymer.

69 The composition of claim 68, wherein the elastomeric polymer contains from 0.1 mol% to 70 mol% of epoxide groups relative to the total number of moles of monomers present in the elastomeric polymer.

70 The composition of claim 69, wherein the elastomeric polymer contains from 0.5 mol% to 60 mol% of epoxide groups relative to the total number of moles of monomers present in the elastomeric polymer.

71 The composition of claim 62, wherein the elastomeric polymer has a mean molecular weight between 2,000 and 1,000,000.

72 The composition of claim 71, wherein the elastomeric polymer has a mean molecular weight between 50,000 and 500,000.

73 The composition of claim 62, wherein the elastomeric polymer is an epoxidized diene homopolymer or copolymer, in which a base polymer structure is derived from one or more conjugated diene monomers, optionally copolymerized with monovinylarenes, polar comonomers, or monovinylarenes and polar comonomers.

74 The composition of claim 73, wherein the base polymer structure is derived from natural rubber, polybutadiene, polyisoprene, styrene/butadiene copolymers, butadiene/isoprene copolymers, styrene/isoprene copolymers, nitrile rubbers, or mixtures thereof.

75 The composition of claim 62, wherein the elastomeric polymer is a copolymer of one or more monoolefins with an olefinic comonomer containing one or more epoxide groups.

76 The composition of claim 62, wherein the elastomeric polymer is a mixture with one or more non-epoxidized elastomeric polymers.

77 The composition of claim 62, wherein the active filler is silica, precipitated silica, pyrogenic silica, alumina, titanium oxide, cellulose fibres, microcrystalline cellulose, zeolites, kaolin, or mixtures thereof.

78 The composition of claim 77, wherein the active filler is precipitated silica, pyrogenic silica, alumina, or mixtures thereof.

79 The composition of claim 62, wherein the active filler is a filler whose surface is modified with hydroxyl groups.

80 The composition of claim 79, wherein the active filler is carbon black at least partially coated with silica.

81 The composition of claim 62, wherein a surface area of the active filler is greater than 40 m<sup>2</sup>/g.

82 The composition of claim 81, wherein the surface area of the active filler is between 80 m<sup>2</sup>/g and 600 m<sup>2</sup>/g.

83 The composition of claim 62, wherein the active filler has a density of active hydroxyl groups greater than 1 group/nm<sup>2</sup>.

84 The composition of claim 83, wherein the active filler has a density of active hydroxyl groups greater than 5 groups/nm<sup>2</sup>.

85 The composition of claim 62, wherein the active filler is present in an amount greater than 20 phr.

86 The composition of claim 85, wherein the active filler is present in an amount between 30 phr and 150 phr.

87 The composition of claim 62, wherein the active filler is mixed with one or more non-active reinforcing fillers.

88 The composition of claim 87, wherein the active filler is at least 50%-by-weight of total filler present in the composition.

89 The composition of claim 62, further comprising one or more of the following additives: antioxidants, protective agents, plasticizers, adhesives, anti-ozonizing agents, curing resins, modifying resins, and fibres.

90 The composition of claim 62, further comprising a lubricant.

91 The composition of claim 90, wherein the lubricant is present in an amount between 2 phr and 100 phr.

92 The composition of claim 91, wherein the lubricant is present in an amount between 5 phr and 50 phr.

93 A process for preparing an elastomeric composition comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl



groups dispersed in the elastomeric polymer, the elastomeric composition being crosslinkable without additional crosslinking agents, the process comprising the step of mixing the active filler with the elastomeric polymer for a predetermined time, to obtain a degree of dispersion of the active filler greater than 90%, and at a predetermined temperature, to avoid pre-crosslinking of the elastomeric composition.

94 The process of claim 93, wherein a temperature of the mixing step is kept below 130°C.

95 The process of claim 94, wherein the temperature of the mixing step is kept below 100°C.

96 The process of claim 95, wherein the temperature of the mixing step is kept below 80°C.

97 The process of claim 93, wherein the active filler and the elastomeric polymer are mixed using an open mixer.

98 The process of claim 93, wherein the active filler and the elastomeric polymer are mixed using an internal mixer.

99 The process of claim 93, wherein the active filler and the elastomeric polymer are mixed using a continuous mixer.

100 The process of claim 97, 98, or 99, wherein a time of the mixing step is greater than 90 sec.

101 The process of claim 100, wherein the time of the mixing step is between 3 minutes and 35 minutes.

102 A process for preparing an elastomeric composition comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups dispersed in the elastomeric polymer, the elastomeric composition being crosslinkable without additional crosslinking agents, and wherein said active filler is dispersed in the elastomeric polymer containing epoxide groups with a dispersion index greater than 90%, the process comprising the steps of mixing the active filler with the elastomeric polymer in the form of an aqueous emulsion or a solution in an organic solvent, and then separating out by precipitation a mixture of the active filler and the elastomeric polymer.

103 A crosslinked manufactured product comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups dispersed in the elastomeric polymer, wherein the manufactured product is crosslinked essentially without additional crosslinking agents, and wherein the active filler is dispersed in the elastomeric polymer with a dispersion index greater than 90%.

104 The product of claim 103, wherein the active filler is dispersed in the elastomeric polymer containing epoxide groups with a dispersion index greater than 95%.

105 The product of claim 104, wherein the active filler is dispersed in the elastomeric polymer containing epoxide groups with a dispersion index greater than 98%.

106 The product of claim 103, obtained by crosslinking, essentially without additional crosslinking agents, a composition comprising an elastomeric polymer

containing epoxide groups and an active filler containing hydroxyl groups dispersed in the elastomeric polymer, the composition having an effective degree of crosslinking equal to at least 65% after no more than 5 minutes of heating at 170°C.

107 A tyre for vehicle wheels, comprising one or more components made of crosslinked elastomeric material, wherein at least one of the components comprises a crosslinked elastomeric material comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups dispersed in the elastomeric polymer, the elastomeric material being crosslinked essentially without additional crosslinking agents, and wherein the crosslinkable elastomeric material has an effective degree of crosslinking equal to at least 65% after no more than 5 minutes of heating at 170°C.

**EVIDENCE APPENDIX TO APPEAL BRIEF**  
**UNDER RULE 41.37(C)(1)(IX)**

1. Varughese *et al.*, *Chemical Attraction Between Expoxidized Natural Rubber and Silica: Studies on Cure Characteristics and Low Temperature Dynamic Mechanical Properties*, Journal of Applied Polymer Science, Vol. 44, pp.1847-1855 (1992). Submitted in IDS dated June 12, 2001, and considered by the Examiner in Office Action dated November 05, 2003.
2. Translation of Japanese Patent Publication No. 07-090123 A. Submitted in IDS dated February 4, 2004, and considered by the Examiner in Office Action dated May 19, 2004.

**RELATED PROCEEDINGS APPENDIX TO APPEAL BRIEF**  
**UNDER RULE 41.37(C)(1)(X)**

**None**

TRANSLATION FROM JAPANESE

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(54) [Title of the invention]

Tyre tread rubber composition

(57) [Abstract]

[Aim]

To provide a tyre tread rubber composition suitable for producing pneumatic tyres of excellent abrasion resistance, rolling resistance and wet skid resistance.

[Constitution]

Tyre tread rubber composition which contains from 30 to 70 parts by weight of silica per 100 parts by weight of rubber component comprising (a) from 20 to 50 parts by weight of natural rubber, (b) from 20 to 40 parts by weight of styrene-butadiene copolymer having a vinyl content, in the butadiene part, of from 35 to 80% by weight and a styrene content of from 10 to 30% by weight and (c) from 20 to 40 parts by weight of epoxidized natural rubber having a degree of epoxidation of from 10 to 60% by weight.

[Scope of the patent claim]

[Claim 1] Tyre tread rubber composition which contains from 30 to 70 parts by weight of silica per 100 parts by weight of rubber component comprising (a) from 20 to 50 parts by weight of natural rubber, (b) from 20 to 40 parts by weight of styrene-butadiene copolymer having a vinyl content, in the butadiene part, of from 35 to 80% by weight and a styrene content of from 10 to 40% by weight and (c) from 20 to 40 parts by weight of epoxidized natural rubber having a degree of epoxidation of from 10 to 60% by weight.

10 [Detailed description of the invention]

[0001]

[Field of industrial use] The present invention relates to a tyre tread rubber composition, more specifically, it relates to a tyre tread rubber composition which simultaneously has satisfactory abrasion resistance, rolling resistance and wet skid resistance.

[0002]

[Prior art] Recent years have seen a demand for cars which conserve energy and resources, and in the tyre industry, research into decreasing resistance to tyre rolling in order to improve car fuel consumption has become very important. It is well known that decreasing the tyre's rolling resistance will lower fuel consumption.

[0003] Using rubber with little hysteresis loss for the tread rubber effectively decreases the rolling resistance of the tyre. However, using rubber of little hysteresis loss tends to decrease the abrasion resistance on wet road surfaces, that is, it tends to decrease the wet skid resistance, and there is an antinomic relationship between two. Consequently, therefore, it has been difficult to simultaneously achieve both satisfactory tyre rolling resistance and satisfactory wet skid resistance.

[0004] Recently it has been shown theoretically that both the tyre rolling resistance and wet skid resistance are related to the viscoelasticity of the rubber composition, and it has been shown that decreasing the hysteresis loss of the tread rubber effectively decreases the rolling resistance when the tyre is running, that is, lowering the dynamic loss ( $\tan \delta$ ) at temperatures of from 50 to 70°C (running temperatures) lowers fuel consumption. However, wet skid resistance has a high deformation frequency, to follow the undulations of the road surface, and so there is a high correlation between viscoelasticity and dynamic loss at low temperatures



(in practice, around 0°C). Accordingly, in order to improve tyre grip, it is necessary to increase  $\tan \delta$  at around 0°C.

5 [0005] It is known that the use of rubber having a low glass transition temperature, such as high cis-polybutadiene and natural rubber, effectively decreases hysteresis loss, but because this lowers  $\tan \delta$  at 0°C, the wet ski resistance decreases and the conventional problem is that low wet skid resistance and low rolling resistance occur simultaneously.

10 [0006] Many recently suggested inventions involve achieving the abovementioned antinomic properties to satisfaction by allowing solution polymerization to proceed. For example, Japanese Unexamined Patent Application Numbers S55-212133 and S56-127650 suggest the use of high-vinyl polybutadiene rubber, and Japanese Unexamined Patent Application Numbers S57-5520 and S57-73030  
15 suggest the use of high-vinyl styrene-butadiene copolymer rubber.

[0007] Moreover, Japanese Unexamined Patent Application Numbers S59-117514, S61-103902, S61-14214, S61-141741 and the like suggest lowering exothermicity by using modified polymers obtained by introducing functional  
20 groups such as benzophenone or isocyanate into the polymer molecular chain. Japanese Unexamined Patent Application Number H-239737 shows that it is possible to achieve low wet skid resistance, low rolling resistance and high abrasion resistance by using styrene-butadiene copolymer rubber (SVR) having a specific styrene chain.

25 [0008] Japanese Unexamined Patent Application Number H3-252431 suggests combining SBR having a specific styrene chain with silane coupling agent, and Japanese Unexamined Patent Application Number H3-252433 suggests that wet skid resistance, rolling resistance and abrasion resistance can all be achieved by  
30 reacting terminal-modified SBR with silica.

[0009]

[Problems to be overcome by the invention] However, none of the abovementioned suggestions always efficiently achieves the abovementioned three  
35 properties to satisfaction. Accordingly, the present invention aims to provide a tyre tread rubber composition in which the abrasion resistance, rolling resistance and wet skid resistance are all improved.

[0010]

[Means of overcoming the problems] The present invention provides a tyre tread rubber composition which contains from 30 to 70 parts by weight of silica per 100 parts by weight of rubber component comprising (a) from 20 to 50 parts by weight of natural rubber, (b) from 20 to 40 parts by weight of styrene-butadiene copolymer having a vinyl content, in the butadiene part, of from 35 to 80% by weight and a styrene content of from 10 to 40% by weight and (c) from 20 to 40 parts by weight of epoxidized natural rubber having a degree of epoxidation of from 10 to 60% by weight.

10

[0011] As a result of diligent research into achieving the abovementioned aim, the present inventors successfully obtained a tyre tread rubber composition in which the abovementioned three properties are simultaneously improved by using styrene-butadiene copolymer rubber (SBR) having a specific microstructure and a specific epoxidized natural rubber (ENR) in a system obtained by compounding silica filler (white carbon) into a rubber blend system comprising natural rubber (NR) and styrene-butadiene copolymer rubber (SBR).

[0012]

[Use] The present invention was designed to achieve the abovementioned aim, and an interesting discovery was made during the investigation into methods for thoroughly dispersing silica filler when silica filler that is conventionally used in the rubber industry is compounded into natural rubber and SBR blend systems.

[0013] According to the present invention, the abovementioned three properties, that is, the abrasion resistance, rolling resistance and wet skid resistance, of tyre tread rubber compositions can all be suitably improved by adding epoxidized natural rubber to an NR/high-vinyl SBR/silica filler system. In the abovementioned system, the ENR does not react with the silica ( $\text{SiO}_2$ ) and so unless the ENR/SBR and  $\text{SiO}_2$  are mixed in portions, the  $\text{SiO}_2$  does not disperse well. However, in the NR/high-vinyl SBR/ENR rubber system of the present invention, the NR is miscible in both the high-vinyl SBR and the ENR, and so the blend of rubber components is a uniform system, and because the NR and  $\text{SiO}_2$  react and disperse well, it is possible to achieve good physical properties.

35

[0014] The SBR is compounded into the tyre tread rubber composition of the present invention at from 20 to 40 parts by weight, preferably from 25 to 35 parts by weight, per 100 parts by weight of starting material rubber component; the styrene content of this SBR is from 10 to 40% by weight, and the vinyl content in

the butadiene part is from 35 to 80% by weight. The terminals of this SBR are preferably modified during polymerization by N,N-dimethylnicotinamide, N,N,N',N'-tetramethylurea, N,N,N',N'-tetramethylaminoacetoamide, N-methyl-2-pyrrolidone, N-methyl-ε-caprolactam, 4,4-bis(diethylaminobenzophenone),  
5 diphenylmethanediisocyanate, and the like.

[0015] The vinyl content in the styrene-butadiene copolymer used in the inventive composition is from 35 to 80% by weight, preferably from 70 to 40% by weight. If  
10 the SBR vinyl content is less than 35% by weight, the miscibility between the natural rubber and the ENR is inadequate and it is impossible to achieve satisfactory dispersion. If said vinyl content exceeds 80% by weight, however, there is a marked decrease in abrasion resistance, which is undesirable.

[0016] The styrene-butadiene copolymer (SBR) used in the present invention is  
15 obtained by copolymerizing styrene and butadiene using a lithium-based catalyst, then modifying the terminals using N,N-dimethylnicotinamide, N,N,N',N'-tetramethylurea, N,N,N',N'-tetramethylaminoacetoamide, N-methyl-2-pyrrolidone, N-methyl-ε-caprolactam,  
4,4-bis(diethylaminobenzophenone),  
diphenylmethanediisocyanate or the like. The bonded styrene content in the  
20 styrene-butadiene copolymer used in the present invention is from 10 to 40% by weight, preferably from 20 to 30% by weight. If the bonded styrene content is less than 10% by weight, the wet skid resistance is low, whereas if it exceeds 40% by weight, the rolling resistance is high, which is undesirable.

[0017] The epoxidized natural rubber (ENR) used in the inventive tyre tread  
25 rubber composition is a commonly known modified rubber which can be produced, for example, by treating natural rubber with hydrogen peroxide and formic acid, and in the present invention, the ENR is present at from 10 to 40 parts by weight, preferably from 25 to 35 parts by weight, per 100 parts by weight of the  
30 total rubber component. The degree of epoxidation of the ENR must be from 10 to 60% by weight, and is more preferably from 25 to 50% by weight. If the degree of epoxidation is less than 10%, the wet skid resistance is inadequate, whereas if it exceeds 50% by weight, the uncured workability becomes extremely problematic.

[0018] The silica filler used in the inventive composition can be any silica (white  
35 carbon) used as a compounding agent for rubber, and the amount used is from 20 to 70 parts by weight, preferably from 25 to 60 parts by weight, per 100 parts by weight of rubber component. If less than 30 parts by weight of silica filler are compounded, the silica filler has little effect and the abrasion resistance

deteriorates, whereas if more than 70 parts by weight are compounded, the breaking properties deteriorate, which is undesirable. The silica filler used in the present invention is preferably a commercial wet-method silica, such as Nipseal VN3 (manufactured by Nippon Silica), Tokuseal U, UR (manufactured by  
5 Tokuyama Soda) or Ultrazil VN3 (manufactured by Degussa).

[0019] Commonly used carbon black may also be used as filler, in addition to the silica, in tyre tread rubber compositions of the present invention. In such cases, the carbon black preferably has reinforcing properties greater than HAF, in view of  
10 abrasion resistance. Specifically, it is preferable to compound from 20 to 70 parts by weight of carbon black having from 80 to 130 m<sup>2</sup>/g of adsorbed nitrogen (N<sub>2</sub>SA) (measured according to ASTM D3037-86) and DBP oil absorption of from 80 to 130 cm<sup>3</sup>/100 g (measured according to ASTM D3493).

15 [0020] Diligent research into mixing methods for the rubber composition of the present invention led to the discovery that when mixing is performed at higher temperatures and speeds than usual, natural rubber undergoes molecular fragmentation more readily, and so more fragment terminal radicals are generated and the reaction with silica is promoted, and better dispersion is achieved.

20

[0021] It should be noted that tyre treads can be produced by including in the tyre tread rubber composition of the present invention the abovementioned starting material rubber and silica, and, optionally, carbon black, and also, if necessary, silane coupling agent, and compounding agents that are commonly used in the  
25 rubber industry, such as sulphur, softening agent, antiageing agent, curing promoter, filler and plasticizer, compounding these to within suitable common ranges for the amounts compounded, then curing by a common method. For example, the sulphur content is preferably no less than 1.2 parts by weight, and more preferably from 1.5 to 3.0 parts by weight, per 100 parts by weight.

30

[0022]

[Working Examples] The present invention is described in more detail below by means of working examples, but the scope of the present invention cannot be said to be limited to these working examples.

35

[0023] In the following working examples, the microstructure of the butadiene part was found by infrared absorption spectrometry and the Hampton-Moreno method. The amount of bonded styrene was measured using the calibration curve prepared

beforehand from the phenol group absorption at  $699\text{ cm}^{-1}$  by infrared absorption spectrometry.

5 [0024] The physical properties of the cured products (100% modulus, TB, EB) were measured according to JIS K6301 (draw rate  $500 \pm 25\text{ mm/min}$ , test temperature  $23 \pm 2^\circ\text{C}$ ). The Lanbourne abrasion test, which is an abrasion resistance test, was performed under the following measurement conditions: 3.0 kg load; 40 m/min wet stone surface speed; slip rate 25% or 35%, performed at a test time of 5 minutes for the 25% test and 2 minutes for the 35% test; falling sand  
10 flow 20 g/min. The measurements were performed at room temperature and the decrease in volume was investigated, and the results were given as indices, taking the Comparative Example 2  $25^\circ\text{C}$  data as 100. The higher the indices, the better the result.

15 [0025] The  $\tan \delta$  value was measured using a spectrometer manufactured by Toyo Seiki Seisakujo (K.K.) at an amplitude of  $\pm 2\%$ , 20 Hz vibration and static strain 10%. The wet skid abrasion resistance was measured according to ASTM E-303-83, at room temperature and  $0^\circ\text{C}$  using a British portable pendrum tester.

20

[0026] Working Examples 1 to 4 and Comparative Examples 1 to 4  
Eight rubber compositions (Comparative Examples 1 to 4 and Working Examples 1 to 4) were prepared by mixing and milling the ingredients shown in Table 1 (parts by weight) using a Banbury mixer and mill roller according to common  
25 methods. Target samples were prepared by press-curing these rubber compositions for 20 minutes at  $160^\circ\text{C}$ , and various tests were performed and their physical properties were measured. The results are shown in Table 1.

[0027]

[Table 1]

Table 1

	Comparative Example				Working Example				(Parts by wt.)
	1	2	3	4	1	2	3	4	Base comp. (parts by wt.)
<u>Comp.</u>									Polymer 100
Natural rubber	-	50	50	50	25	25	25	25	Zinc flours 3
SBR1 <sup>*1</sup>	100	50	50	-	-	-	-	-	Stearic acid 2
SBR2 <sup>*2</sup>	-	-	-	-	-	-	35	-	Antiagging agent 2
SBR3 <sup>*3</sup>	-	-	-	-	-	-	-	35	Oil 8
SBR4 <sup>*4</sup>	-	-	-	50	35	25	-	-	Curing promoter <sup>*5</sup> 0.7
ENR <sup>*5</sup>	-	-	-	-	40	50	40	40	Sulphur 1.7
Silica <sup>*6</sup>	-	-	25	25	25	25	25	25	
Carbon black <sup>*7</sup>	50	50	25	25	25	25	25	25	
Silane coupling agent <sup>*8</sup>	-	-	3	3	3	3	3	3	
100% modulus	28	25	28	33	41	40	43	41	
Tensile strength (kg/cm <sup>2</sup> )	248	242	238	267	284	273	259	265	
Extension at break (%)	441	440	437	425	470	465	440	453	
tan δ °C	0.268	0.270	0.270	0.301	0.514	0.562	0.627	0.595	
tan δ 60°C	0.130	0.141	0.130	0.089	0.142	0.148	0.142	0.146	
wet skid room temp.									
wet skid 0°C	88.5	88.5	88.2	89.3	93.7	93.4	92.9	92.3	
0°C	90.0	90.0	91.0	91.7	92.3	91.0	88.6	89.8	
Lanbourn abrasion									
25% (Index)	113	100	112	107	105	102	96	100	
35%	108	96	113	114	110	106	98	102	

5

[0028] [Notes for Table 1]

\* 1: Bonded styrene content 23.5%, vinyl content 14.9%

\* 2: Bonded styrene content 13.8%, vinyl content 78.4%, 4,4'-bis(diethylamino-benzophenone) modified terminals

10

- \* 3: Bonded styrene content 20.6%, vinyl content 66.5%, 4,4'-bis(diethylamino-benzophenone) modified terminals
- \* 4: Bonded styrene content 23.2%, vinyl content 37.3%, N-methyl-2-pyrrolidone modified terminals
- 5 \* 5: ENR (manufactured by Kumplan Guthrie Berhard (Malaysia)) having a degree of epoxidation of 25% by weight, obtained by modifying NR
- \* 6: Nipseal VN3
- \* 7: HAF (N<sub>2</sub>SA: 88 cm<sup>2</sup>/g, DBP oil absorption: 110 cm<sup>3</sup>/100 g)
- \* 8: bis(3-triethoxysilylpropyl)tetrasulphide
- 10 \* 9: N-cyclohexyl-2-benzothiazylsulphenamide

[0029] As is clear from the results shown in Table 1, Comparative Examples 1 and 2 relate to systems obtained by adding carbon black to a natural rubber system or a natural rubber/SBR system, but neither exhibit satisfactory wet skid resistance.

15 Comparative Example 1 relates to a natural rubber/carbon black system, and as the T<sub>g</sub> is low, the wet skid resistance is not satisfactory. Comparative Example 2 relates to a universally used SBR/natural rubber system, but here too the wet skid resistance is not satisfactory. Moreover, the systems of Comparative Examples 1 and 2 both have high tan  $\delta$  values, 60°C, and so they are also undesirable in terms

20 of their rolling resistance.

[0030] Comparative Example 3 relates to a natural rubber/SBR/silica system, but as the rubber component is a natural rubber/universally used SBR system which contains no ENR, the wet skid resistance is unsatisfactory. Comparative Example 4

25 relates to a natural rubber/SBR system, but as the vinyl content in the SBR is low, the wet skid resistance is unsatisfactory.

[0031] Working Examples 1, 2, 3 and 4, however, relate to systems of the present invention obtained by combining natural rubber, high-vinyl SBR, ENR and silica,

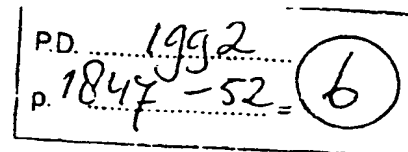
30 and so a balance is achieved between the wet skid resistance, tan  $\delta$  (60°C) and the abrasion resistance, and the modulus and breaking strength are also excellent.

[0032]

[Advantages of the invention] As described above, tyre tread rubber compositions

35 obtained by combining natural rubber, high-vinyl SBR, ENR and silica according to the present invention simultaneously exhibit high wet skid resistance, low rolling resistance and high abrasion resistance, and so they are suitable for tyre production.

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# Chemical Interaction Between Epoxidized Natural Rubber and Silica: Studies on Cure Characteristics and Low-Temperature Dynamic Mechanical Properties

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## SYNOPSIS

The unusual reinforcement mechanism exhibited by silica in epoxidized natural rubber (ENR) may be attributed to the specific chemical interaction or the chemical cross-linking taking place between silica and the epoxy groups while heating the mix. Evidence for the higher interaction is established through rheometric studies conducted at 180°C and changes in the dynamic mechanical characteristics studied over a wide temperature range using a dynamic viscoelastometer for the heated and unheated silica-filled mixes.

## INTRODUCTION

Epoxidized natural rubber (ENR) has been introduced to the elastomeric world as a modified form of natural rubber (NR) with high application potential as an oil-resistant, air-impermeable, and highly damping rubber.<sup>1-5</sup> Recent studies conducted by De et al. showed that ENR has potential as a chemically reactive rubber, which can cross-link with other polymers having functional groups such as chloroprene, chlorosulfonated polyethylene, poly(vinyl chloride) carboxylated nitrile rubber, etc.<sup>6-9</sup> Because of the high cross-link densities, when these polymers are reacted, external, conventional curing agents are not required for the curing of these blends. The functionally active epoxy group of ENR is responsible for such interactions. The vulnerability of epoxy groups for such chemical reactions led us to the present investigation to find out the special mechanism responsible for the high reinforcement of silica in ENR. It is known that the active silanol groups can interact with other functional groups containing polymers like carboxylated nitrile rubber. Physical property studies conducted on silica-filled ENR systems showed that there is a marked difference in the interaction mechanism of

ENR and silica compared to other fillers.<sup>10</sup> Silica reinforces ENR to an extent similar to the black-filled systems. The interaction or reinforcement mechanism operating in the case of ENR and silica could not be explained properly based on the physical property studies alone. The present study is the result of our experiments on silica-filled ENR systems to find out whether there is any cross-linking between the two, through rheometric studies and low-temperature-to-high-temperature dynamic mechanical property studies in the absence of any conventional curing agents.

Curing agents were avoided to elucidate the interaction mechanism between silica and ENR alone, which may otherwise become complex.

## EXPERIMENTAL

### Materials and Mixing

A 50 mol % epoxidized NR is used for the study. Formulations and details of materials used are given in Table I. Table II contains conditions followed for the dynamic mechanical analysis. Natural rubber (NR), ISNR-5 grade, is also used in one mix for comparison. Mixing was carried out on a laboratory-size two-roll mixing mill (32.5 × 15 cm). Total mixing time has been kept minimum to avoid sticking of the compound to the mill rolls. Care was taken to see that the mill-roll temperatures are not ex-

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Table I Details of Materials Used

Material	Details
Epoxidized natural rubber (ENR)	50 mol % epoxidized, supplied by Malaysian Rubber Producers' Research Association, Brickendonbury, U.K.
Silica	Ultrasil VN3, supplied by Bayer India Limited, Bombay
Bis(triethoxy silyl propyl) tetrasulfide (Si-69)	Manufactured by Degussa, Germany

ceeding the set temperatures to avoid any cross-linking during mixing.

#### Sample Preparation and Testing

Cure studies were carried out on a Monsanto Rheometer (model 100S) at 180°C. Samples for dynamic mechanical analysis were prepared in dimensions of 7 × 0.4 × 0.3 cm by compression-molding at 180°C for 1 h. Unheated or uncured mixes were press-molded at 100°C for a limited time to get the proper sample dimensions before testing. One mix was prepared with heated silica. For this, silica was heated in an oven at 120°C for 6 h before it was mixed with the rubber. All the test samples were conditioned at room temperature for a minimum period of 24 h before the tests were carried out.

Dynamic mechanical analysis was done on a dy-

namic viscoelastometer (Rheovibron, model DDV-III-EP, Orientec Corporation, Japan) at a temperature range of -100°C to +250°C at a heating rate of 1°C/min at 3.5 Hz frequency.

## RESULTS AND DISCUSSION

### Cure Characteristics

Rheographs of different mixes are given in Table II and are shown in Figure 1. Mix A is pure gum ENR-50. Mix B contains 50 phr unheated silica. It is seen from these two graphs that there is a rise in torque values at 150°C for mix B, whereas mixes containing 50 phr ISAF in ENR-50 (mix H) and 50 phr silica in NR (mix I) did not show any such change in the torque values. Mix A was kept in the rheometer for

Table II Formulations and Conditions Followed

Mix Designations	Ingredients and Conditions Followed
A	ENR-50, 100 phr (gum)
B	ENR-50, 100 phr; silica, 50 phr; unheated
C	ENR-50, 100 phr; silica, 50 phr; Si-69, 2 phr; unheated
D	Mix B heated for 1 h at 180°C
E	Mix C heated for 1 h at 180°C
F	ENR-50, 100 phr; heated silica, 50 phr; heated for 1 h at 180°C
G	ENR-50, 100 phr; silica, 50 phr; Si-69, 2 phr; Na <sub>2</sub> SO <sub>4</sub> , 0.2 phr; heated for 1 h at 180°C
H	ENR-50, 100 phr; C-black (ISAF), 50 phr
I	NR, 100 phr; silica, 50 phr

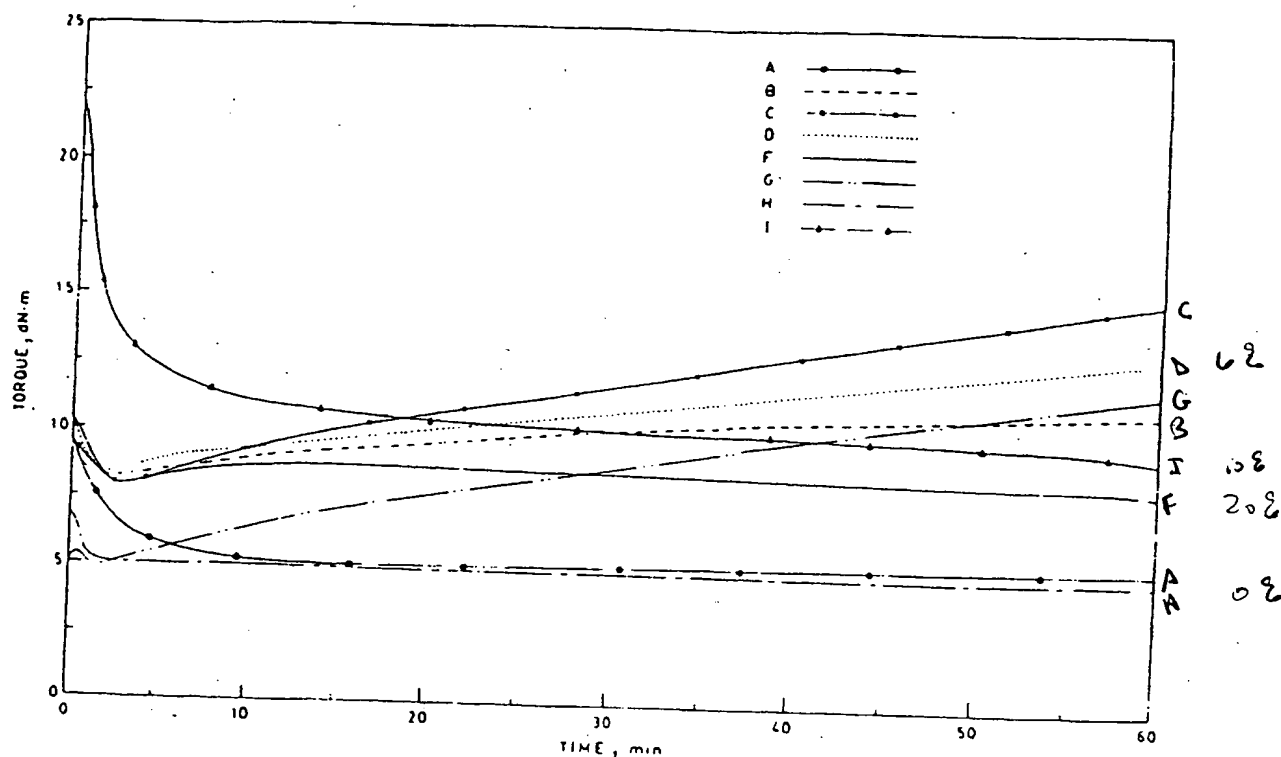


Figure 1 Effect of heating of silica-filled ENR-50 mixes. rheometer curves at 180°C.

1 h at 180°C to determine whether there was any hardening or gelling taking place in the ENR on heating. The resultant plateau curve ruled out any such chances of hardening in ENR at 180°C. This indicates that a chemical reaction is taking place between silica and ENR-50 and that there is slight cross-linking. Generally, the interactions between a filler and a polymer are not high enough so that cross-linking can be detected through a rheometer torque rise. It was expected that a chemical reaction is taking place between the silanol groups and epoxy groups during heating of the mix.

Previous studies on physical properties showed that silica-filled ENR exhibit properties comparable to that of black-filled vulcanizates.<sup>8</sup> This clearly gives evidence for the higher reinforcing ability of silica in ENR. Studies on polymers with functionally active side groups proved that they enter into chemical cross-linking with the silanol groups of silica. Silica filler in epoxy resin is also found to be chemically active. The higher reinforcement observed in the case of silica-filled ENR was presumed to be a similar interaction mechanism to that of black-filled vulcanizates. However, a comparatively good number of cross-links (considerable rise in rheometric torque, nonsticky and transparent vulcanizates) are

present in the silica-filled vulcanizates even in the absence of any conventional curing agents.

Here, heating of the mixes should be treated separately from the vulcanization of samples. Usually, vulcanization is done for a much shorter period and at a lower temperature. This indicates that for the cross-linking to take place between the epoxy and silanol groups a higher activation energy is required. Hence, while considering the reinforcement characteristics of conventionally cured silica-filled vulcanizates, it should be taken into account that the chemical interaction under such conditions is comparatively poor.

With 2 phr Si-69 in mix B, the rheometer torque rises further (mix C, Fig. 1). The cross-linking action is further accelerated by the presence of Si-69. Si-69 can cure elastomers because of its chemical structure. Here, also, the observed rise in torque can be attributed to this. Silica generally forms cross-links with elastomers through the silanol groups. To prove this effect, silica was heated in an oven for 6 h at 120°C (percentage weight loss = 6.5) and then mixed with ENR (mix F). Mild heating of silica at 105°C can result in the loss of adsorbed water molecules from its surface and can result in a strained siloxane structure (Figure 2).<sup>11</sup> This may

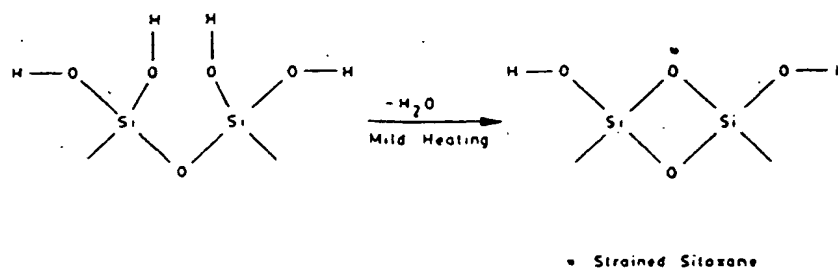


Figure 2 Effect of mild heating on silica-strained siloxane formation.

result in the reduction in the number of geminal silanol groups available on the silica surface that enter into chemical cross-linking with the epoxy

groups. Subsequently, there was a retardation effect in the cross-linking rate (curve F, Fig. 1).

Similarly, while cross-linking, some water mol-

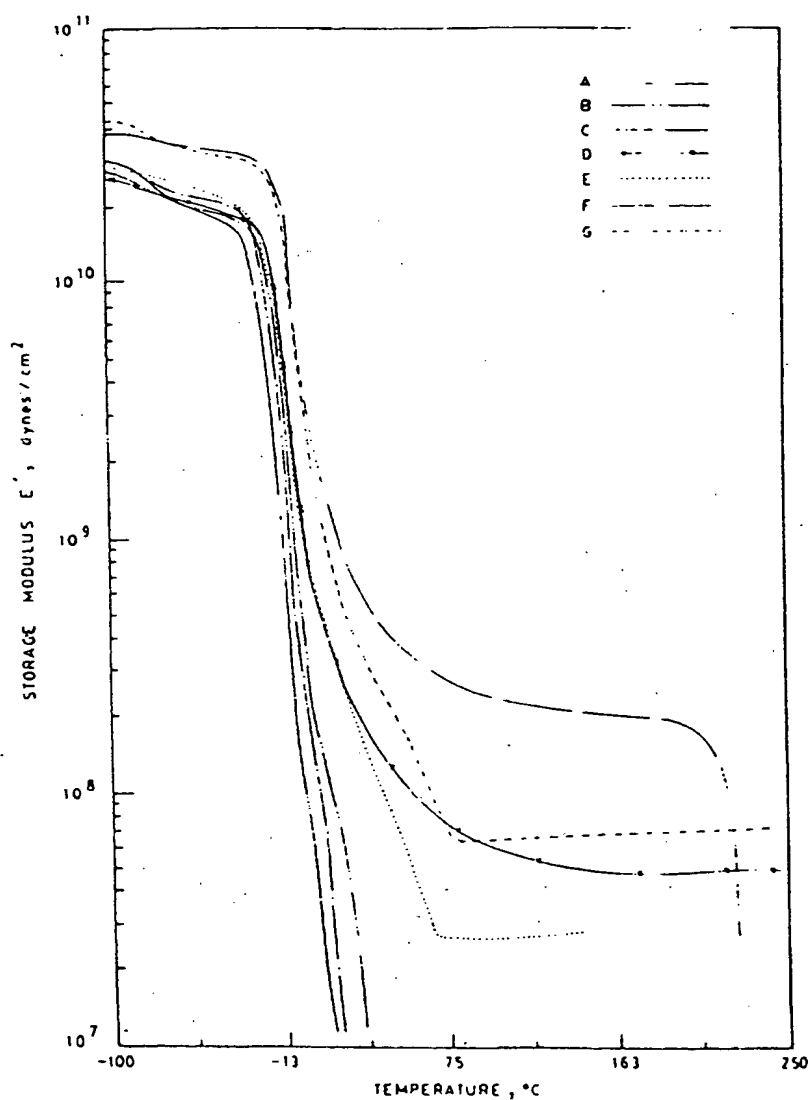


Figure 3 Storage modulus,  $E'$  vs. temperature plots at 3.5 Hz. Effect of silica on ENR-50 under conditions given in Table II.

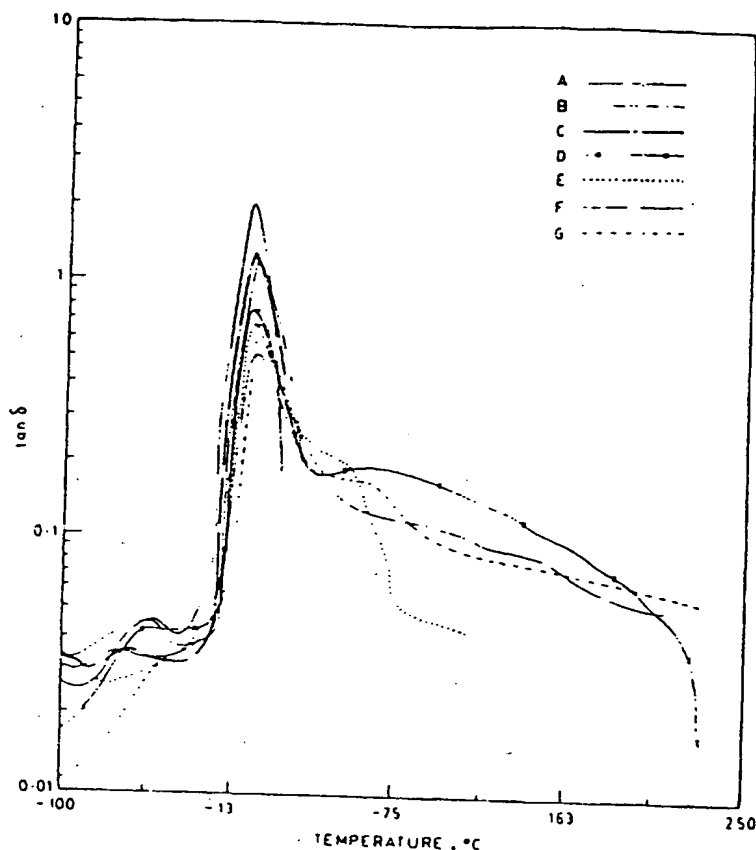


Figure 4 Loss angle  $\tan \delta$  vs. temperature plots at 3.5 Hz. Effect of silica on ENR-50 under conditions shown in Table II.

ecules may be eliminated as a side-reaction product. We have tried to remove these water molecules *in situ* by adding a catalytic amount of anhydrous sodium sulfate into the mixture while mixing. The reaction rate was expected to increase with this. On the contrary, mix G registered a slower cure rate. The reaction mechanism still needs detailed study.

#### Dynamic Mechanical Properties

Figures 3 and 4 show the effect of silica filler on the dynamic mechanical properties (low temperature to high temperature) of ENR-50. Both heated and unheated samples were analyzed. Studies carried out on carbon black and silica- and clay-filled rubbers showed that there is a striking influence of the interaction parameters of a filler and polymer on the storage modulus values,  $E'$ , and loss tangent,  $\tan \delta$ , loss tangent peak height, spread, and the glass transition temperature,  $T_g$ , etc.<sup>12-15</sup> The effect of varying filler-rubber interaction parameters on  $E'$  values is shown in Figure 3. Mixes A, B, and C were unheated, and mixes D, E, F, and G were compression-molded

at 180°C for 1 h. Heated samples showed an obvious increase in the spread of the  $E'$  curve and the modulus values were higher enough to withstand a higher temperature range, unlike the unheated mixes.

The presence of a stronger network structure is indicated in the case of heated samples due to the cross-linking or strong chemical interaction.<sup>16</sup> The strain applied on the system could easily be dissipated between the cross-link junctions due to the strong interchain linkages, whereas mix E showed a lower heat resistance for the storage modulus values. This may be due to the slight plasticizer action of Si-69.

High temperature  $E'$  values were observed in the case of mixes F and G. When the filler is heated, its surface morphology is changed and the surface energy will subsequently show a change. This changed surface structure may result in an increase in the filler modulus alone. Hence, the rise in  $E'$  values in the case of mix F is reasonable according to this probability. Addition of sodium sulfate may also be causing changes like this to account for the high-temperature  $E'$  values. The influence of filler on the

**Table III** Glass Transition Temperature and  $\tan \delta_{\max}$  Values

Mix Designations	Glass Transition Temperature (°C at 3.5 Hz)	$\tan \delta_{\max}$
A	-5	1.90
B	-4	1.15
C	-6	1.22
D	-4	0.74
E	-5	0.68
F	-2	0.51
G	-1	0.66

dynamic mechanical properties is negligible in the case of unheated mixes. However, the nature of the  $E'$  curves gives strong proof for the existence of a stronger network in the case of heated mixes.

The filler-rubber interaction phenomenon is more clearly explained through the nature of the loss tangent curves (Fig. 4).  $\tan \delta$  peak height, spread, and location can give a valuable account of the changes occurring in the polymer phase on the addition of filler and cross-links. The  $\alpha$ -relaxation peak height gives an indication of the total free volume available in the system. The molecular chain motions become maximum at the glass-rubber transition state. Hence, if any restriction to the free chain mobility is introduced to the polymer phase, it will be reflected in the various aspects of the  $\alpha$ -relaxation peak or the loss tangent peak. When the interaction between the rubber and filler increases, either more and more polymer chains will be adsorbed onto the filler surface or changes may occur in the filler structure, so that the occluded or bound rubber amount may change.

Figure 4 shows that the addition of the silica-to-ENR phase reduced the gum polymer  $\alpha$ -relaxation peak height. The  $\tan \delta_{\max}$  and  $T_g$  values are given in Table III. When the interaction rate or cross-linking is further raised as in the case of mix C,  $\tan \delta_{\max}$  values reduced further. In the case of mixes D, E, and G, a second hump can be seen above the  $\alpha$ -relaxation peak temperature. This shows a higher amount of adsorbed rubber present in the system, which requires a higher energy for the relaxation of the molecular chains when the mixes are heated.<sup>12,15</sup>

This gives additional evidence to the fact that heating of silica-filled ENR changes the filler-rubber interaction parameters.

## CONCLUSION

Epoxidized natural rubber, 50 mol %, is found to have high interaction with the silanol groups of silica filler. The interaction rate increases with the addition of a silane coupling agent as evidenced through rheometric and dynamic mechanical analysis. Dynamic mechanical analysis of heated and unheated mixes gave additional proof to the nature of interaction between ENR and silica in the absence of any conventional vulcanization agents.

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